Characterization of Nanomaterials: In Situ Electron Microscopy

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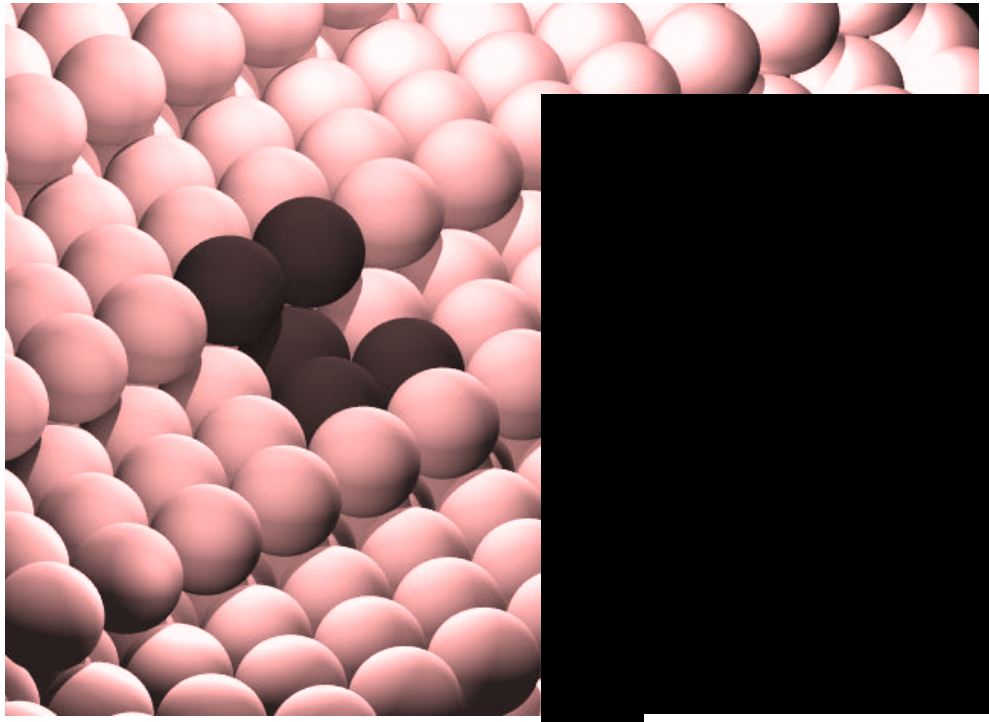
Thomas W. Hansen

Characterization of Nanomaterials: *In Situ* Electron Microscopy

Holy Grail: Can we Observe an Active Catalyst/Nanoparticle?



b_5 sites on the (105) surfa[illegible] sites were proposed to be the active sites for N_2 splitting (van Hardeveld and von Montfoort Surf. Sci. 4 (1966) 396). Figure from T.W. Hansen *et al. Catal. Lett.* **84** 7 (2002).

- Materials respond **dynamically to changes in environment**

[redacted]

The little guy cannot know we are watching…

vs. gaseous atmospheres

adsorption/desorption

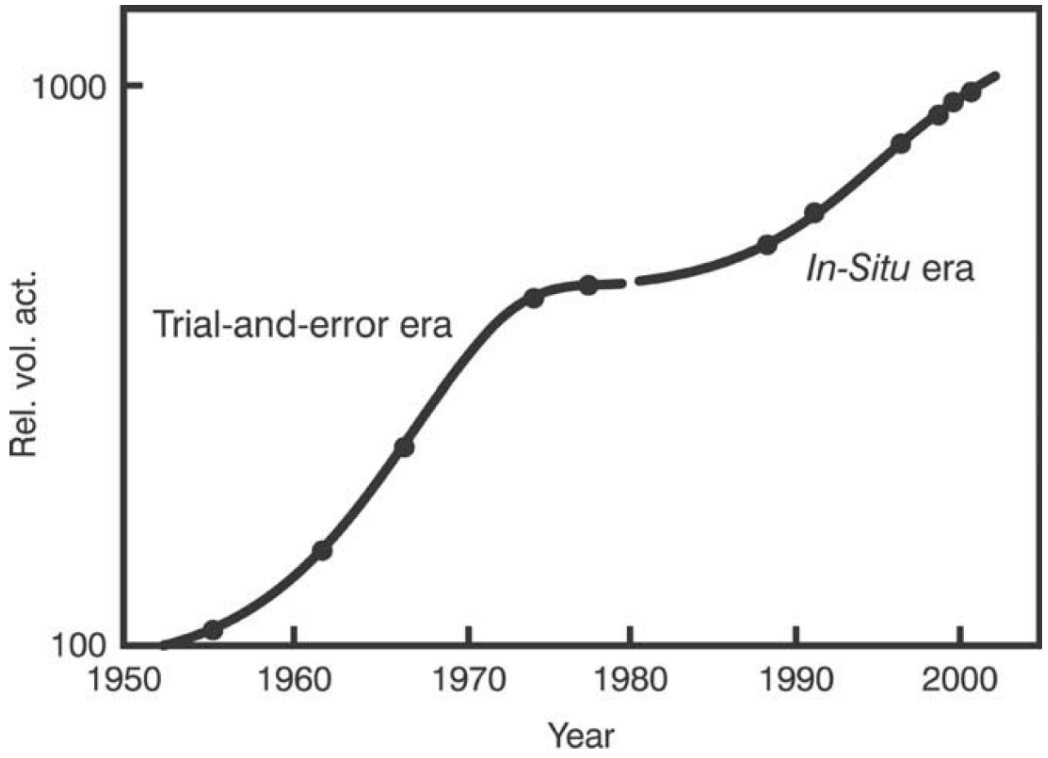
croscopy does not

r operational environment ->

sites are normally not active in vacuum

- Essential for establishing structure-activity correlations

In Situ Techniques



Evolution of activity of industrial HDS catalysts,

B.M. Moyse, World Refining Jan/Feb (2001) 28

H. Topsøe, J. Catal. 216, 155 (2003)

- *In situ* XRD
  - Phase determination
  - Good for large areas
- *In situ* EXAFS, FTIR
  - Coordination
  - Chemical bonding
- Average values
  - No local information
- *In situ* TEM
  - Gives local information
- Etc…

In Situ Microscopy is not New…

Aus dem Laboratorium für Elektronenoptik der Siemens & Halske AG., Berlin-Siemensstadt.

Beitrag zur übermikroskopischen Abbildung bei höheren Drucken.

Von E. Ruska.

(Eingegangen am 13. Mai 1942)

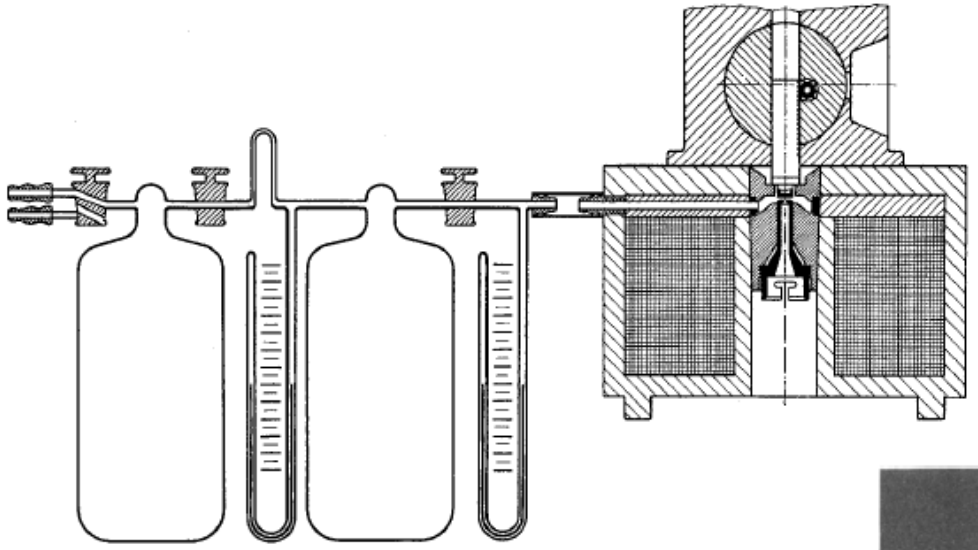


Fig. 1. Schematischer Querschnitt durch die Versuchsanordnung.

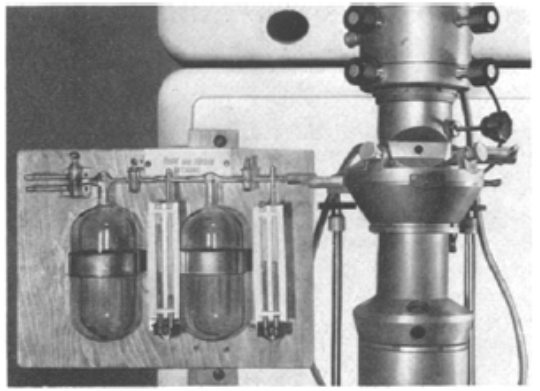
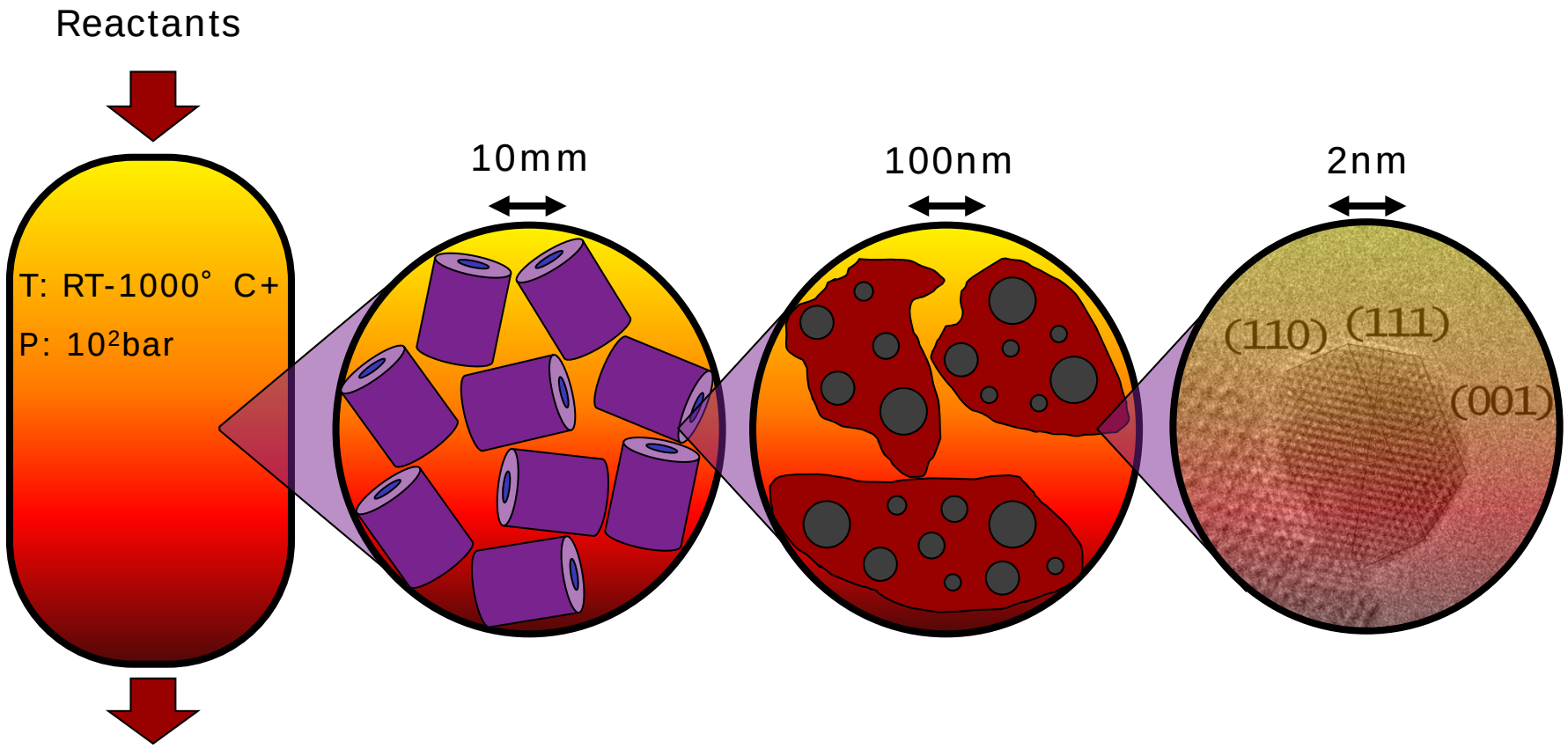


Fig. 3. Ansicht der Einrichtung für Gaszufuhr am Siemens-Übermikroskop.

A Look Inside the Reactor



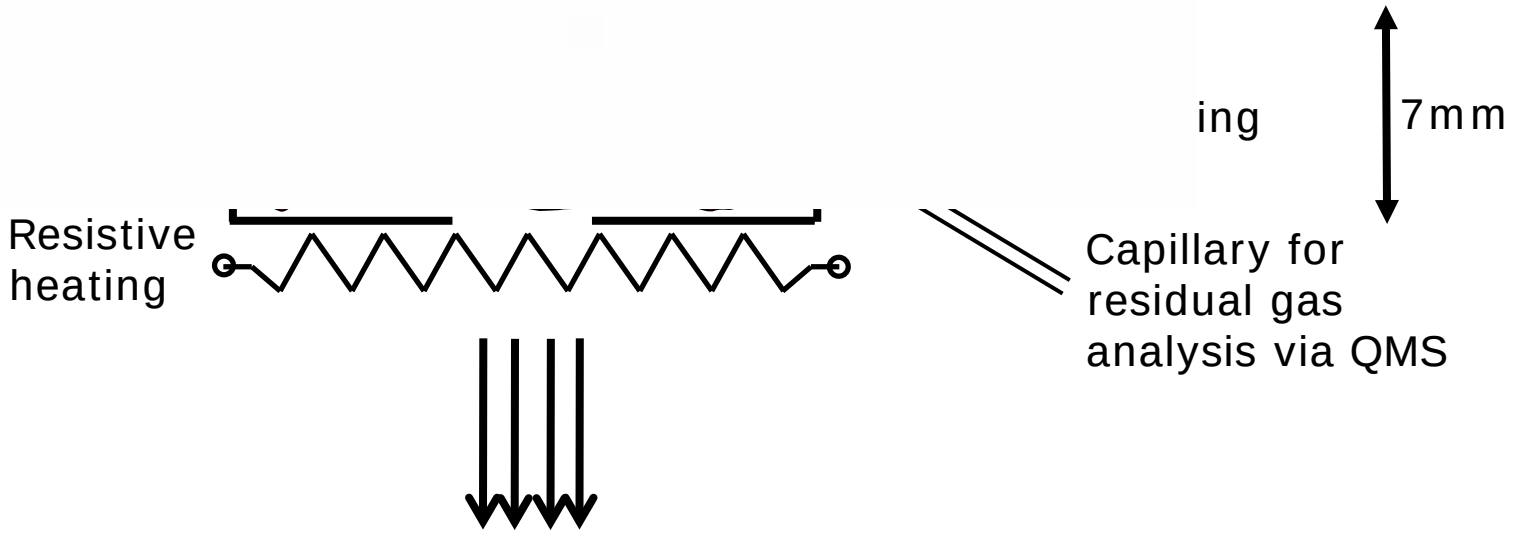
The Environmental Cell

- not really a cell…

- Main pu
  the gas
  possibl

making

Reacti
gas



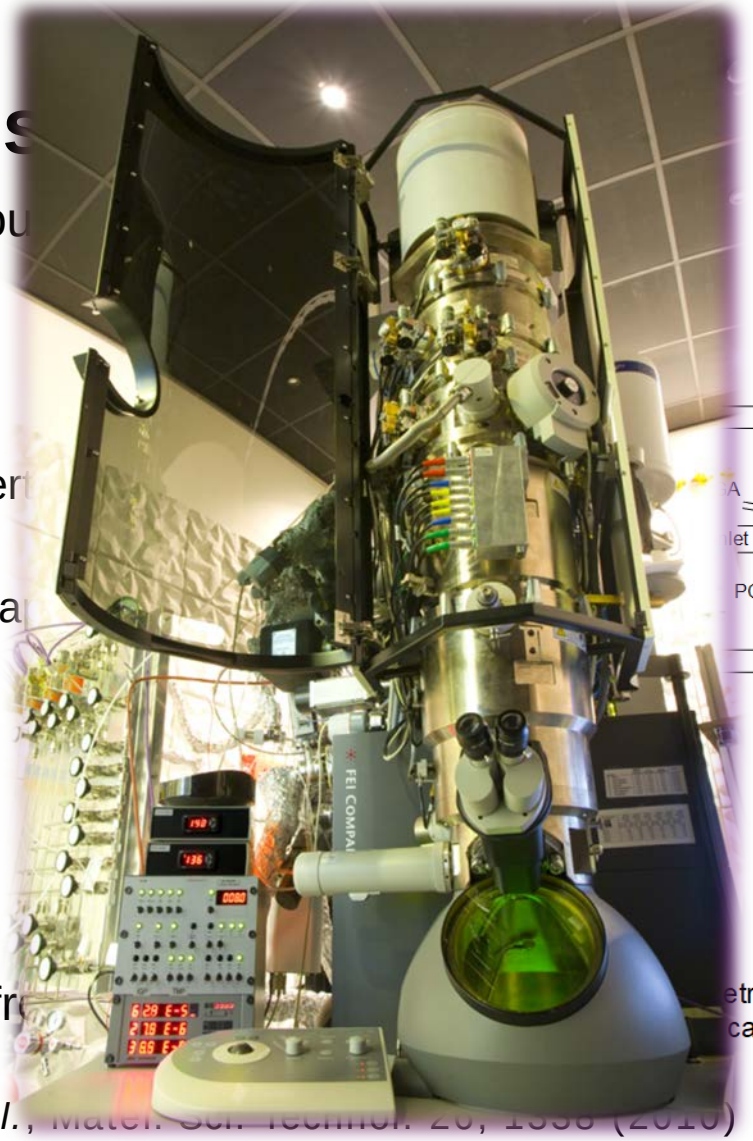
ETEM
- Column Des

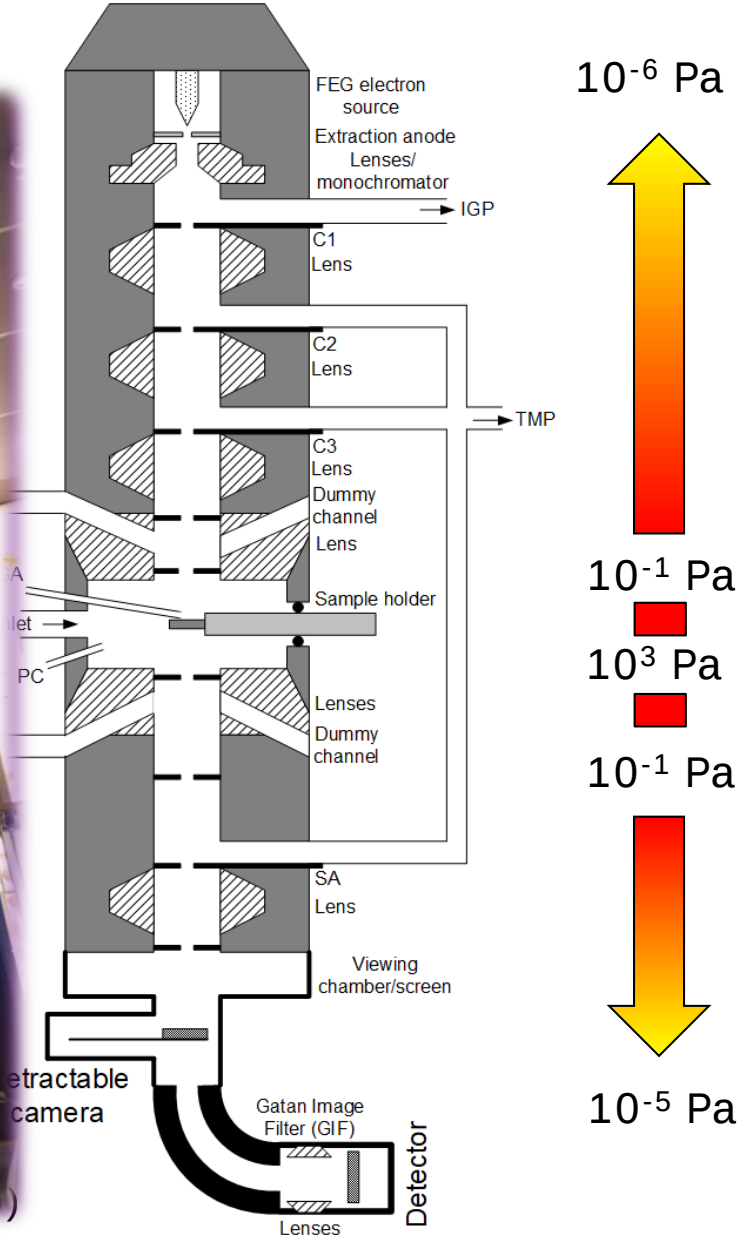
- Monochromated FEG electron sou

- Differential pumping system
  1. Gas is leaked in
  2. First set of diffusion limiting aper
  3. Turbo molecular pump
  4. Second set of diffusion limiting a
  5. Turbo molecular pump
  6. Ion getter pump (IGP)

- Direct line of sight!

- Conceptually not much different fr
  systems



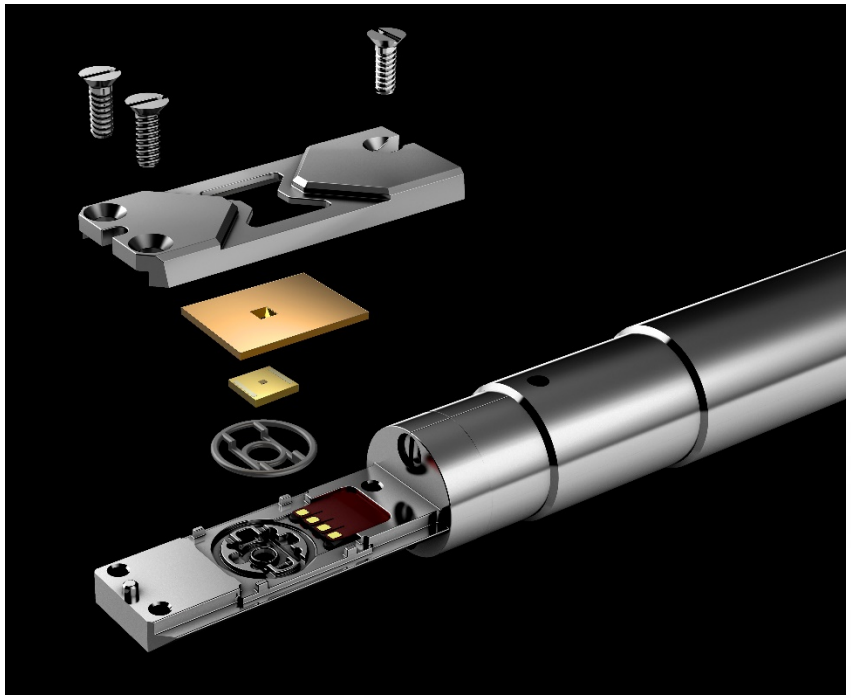


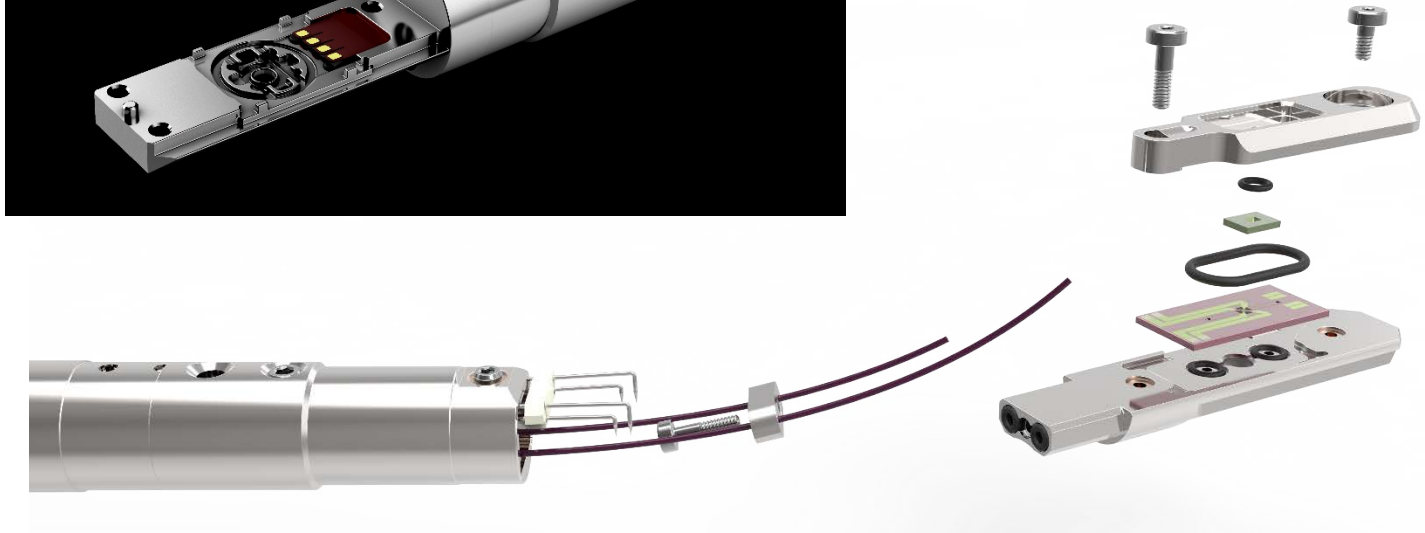
T. W. Hansen *et al.*, Mater. Sci. Technol. 26, 1338 (2010)

T. W. Hansen and J. B. Wagner Eds.: *Controlled Atmosphere Transmission Electron Microscopy*, Springer (2016)

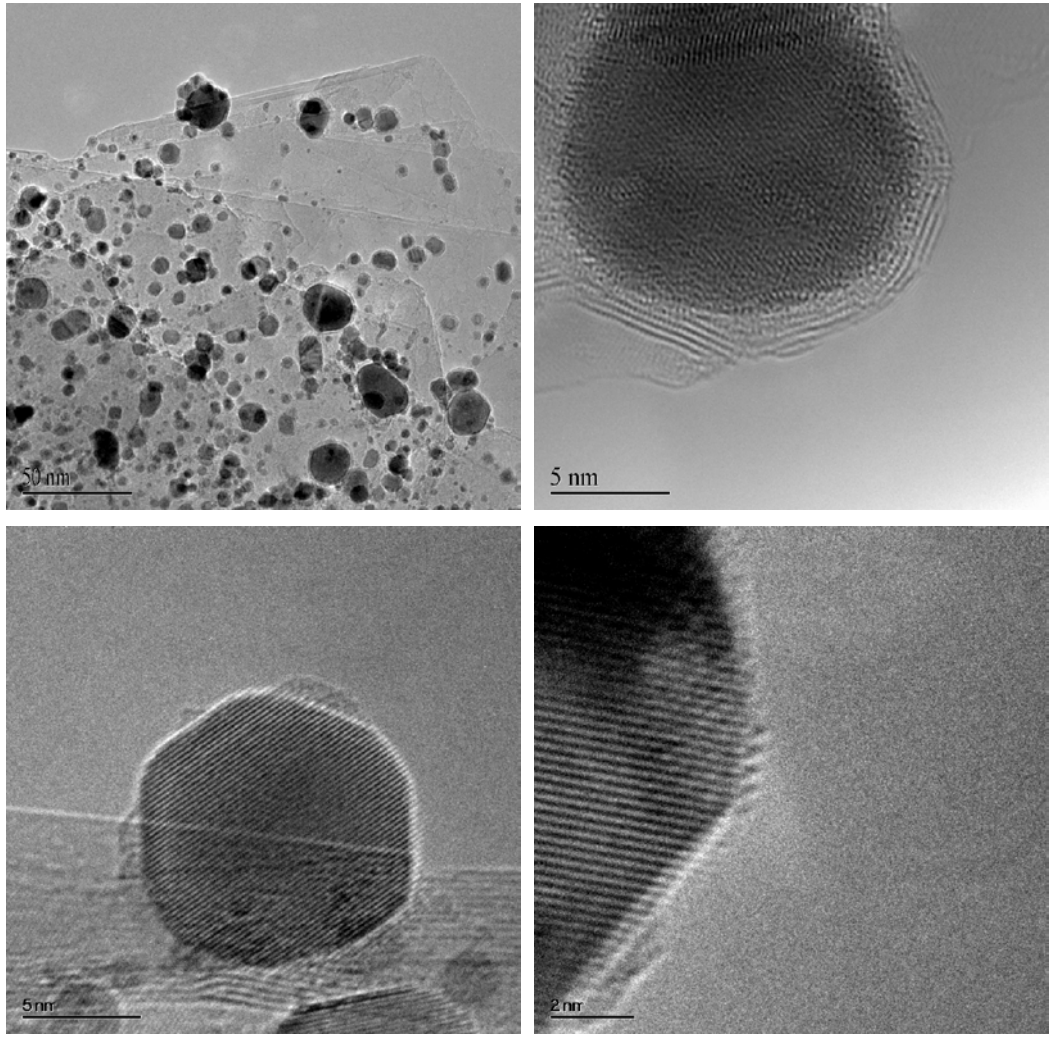
Closed Cells Systems

- Gas encapsulated between electron transparent windows
- Can sustain gas pressures above 1 atm
- MEMS based heater
- Low drift





Why do We Want to do *In Situ* Microscopy?



Ru/BN-Ba

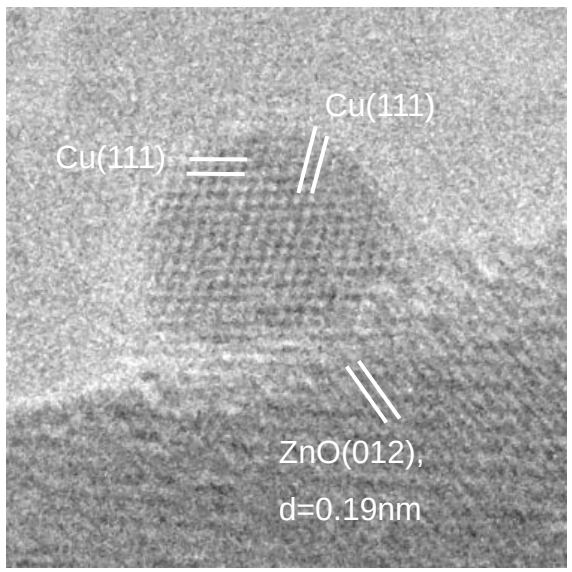
Vacuum

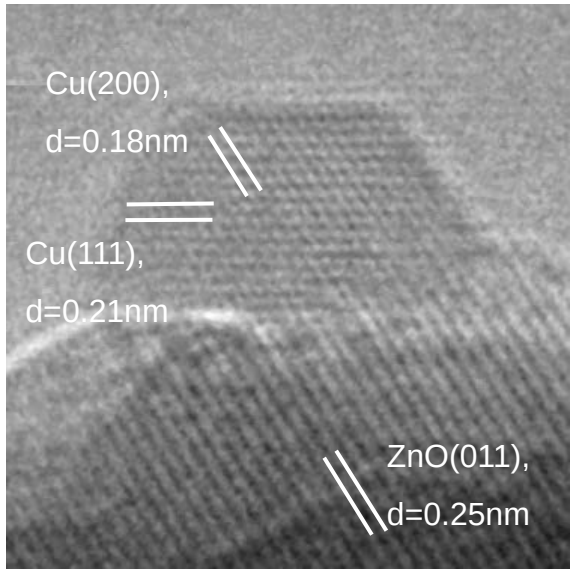
3:1 H_2:N_2 ca. 300 Pa, 450° C

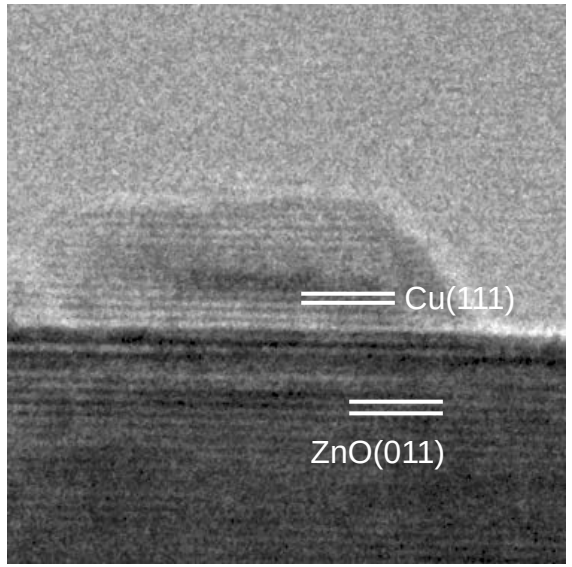
T. W. Hansen *et al.*, *Science* **294**, 1508 (2001)

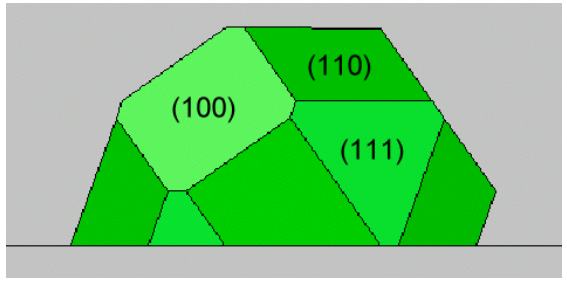
Equilibrium Shape vs. Gas Composition, Cu/ZnO

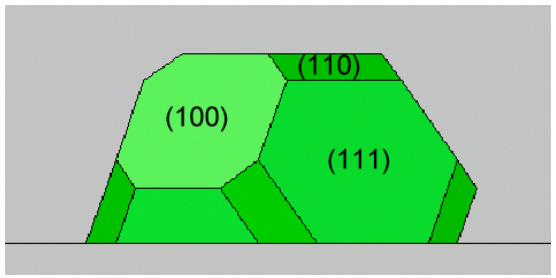
H_2/H_2O ⇄ H_2 ⇄ H_2/CO

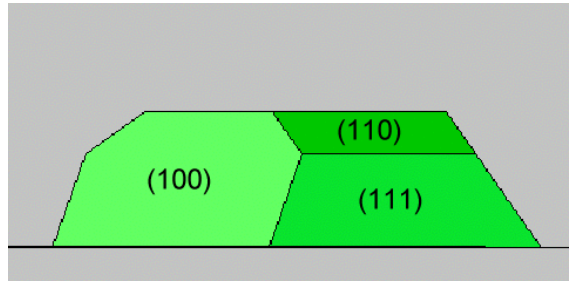












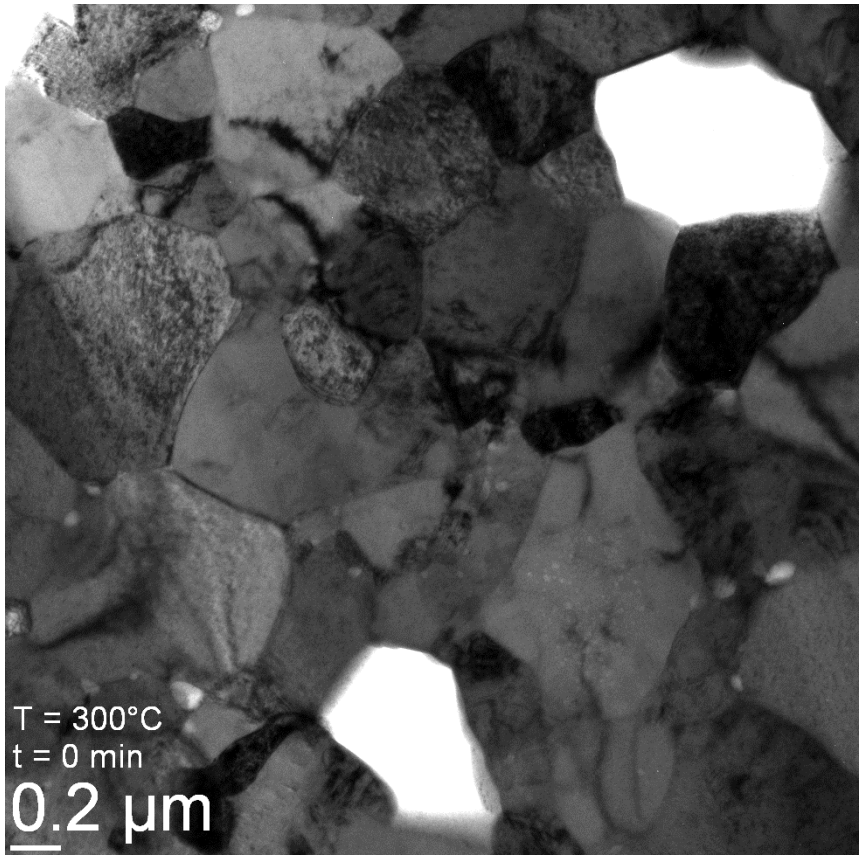
150 Pa, H_2/H_2O=3/1, 220°C | 150 Pa, 220°C | 150 Pa, H_2/CO=95/5, 220°C

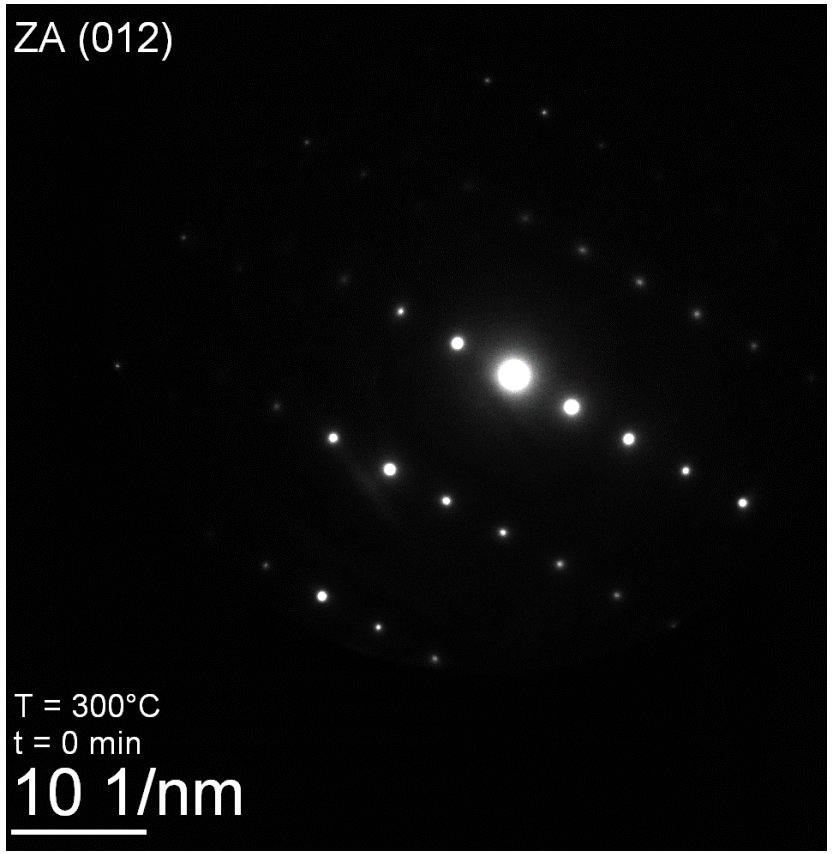
More oxidizing ⟷ More reducing

J. B. Wagner, PhD thesis (2002)

P. L. Hansen *et al.*, *Science* **295**, 2053 (2002)

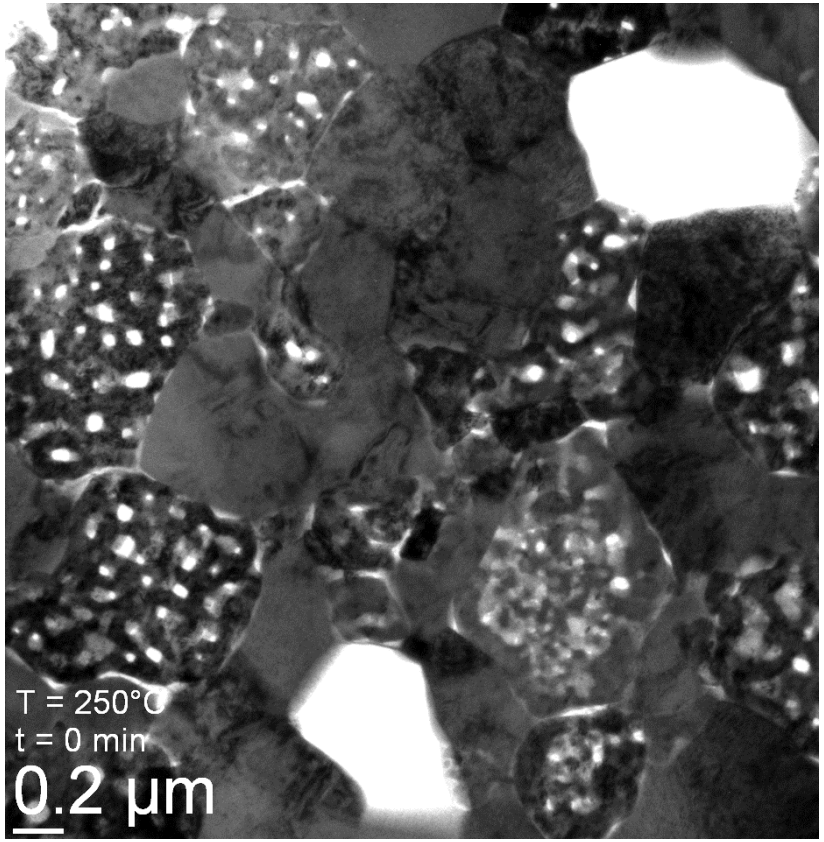
In Situ Red(ox) Process in a Fuel Cell

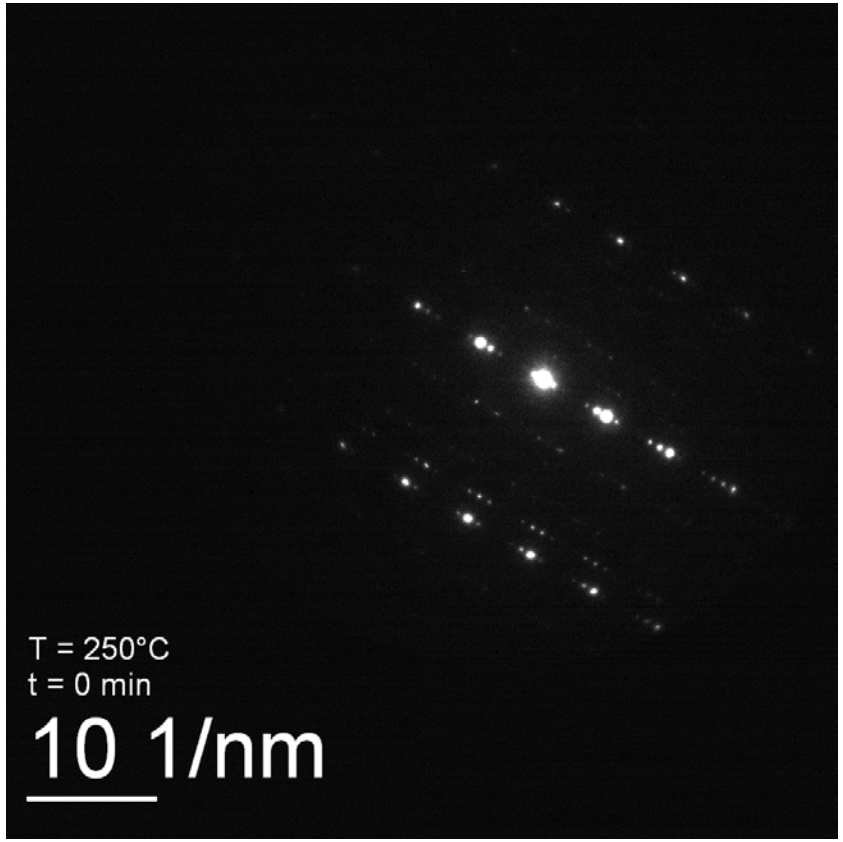




Q. Jeangros, TWH *et al.*, *Acta Mater.* **58**, 4578 (2010)

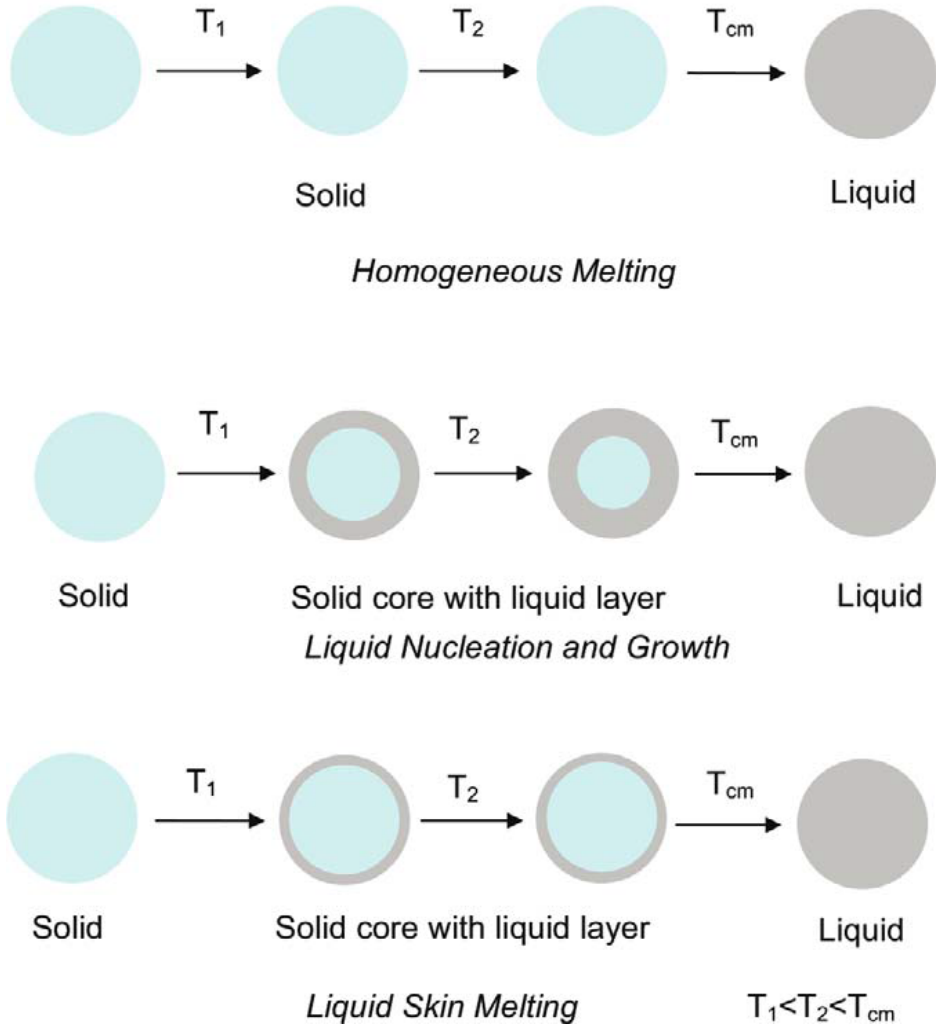
In Situ (Red)ox Process in a Fuel Cell





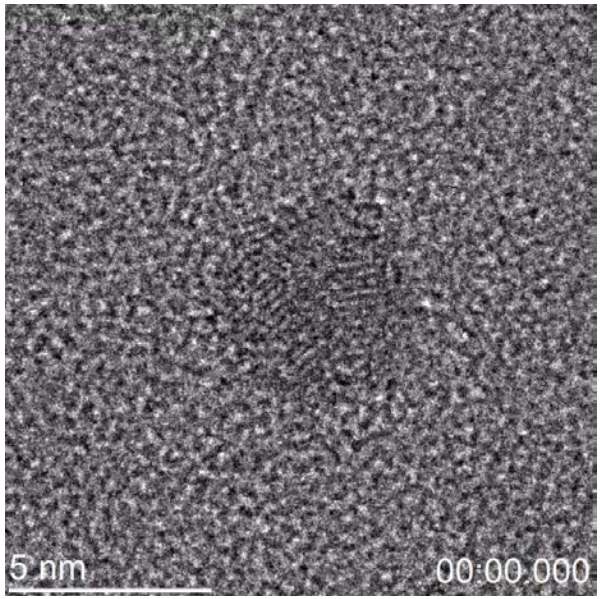
Q. Jeangros, TWH *et al.*, *Acta Mater.* **58**, 4578 (2010)

Melting of Metal Nanoparticles
- Melting Models



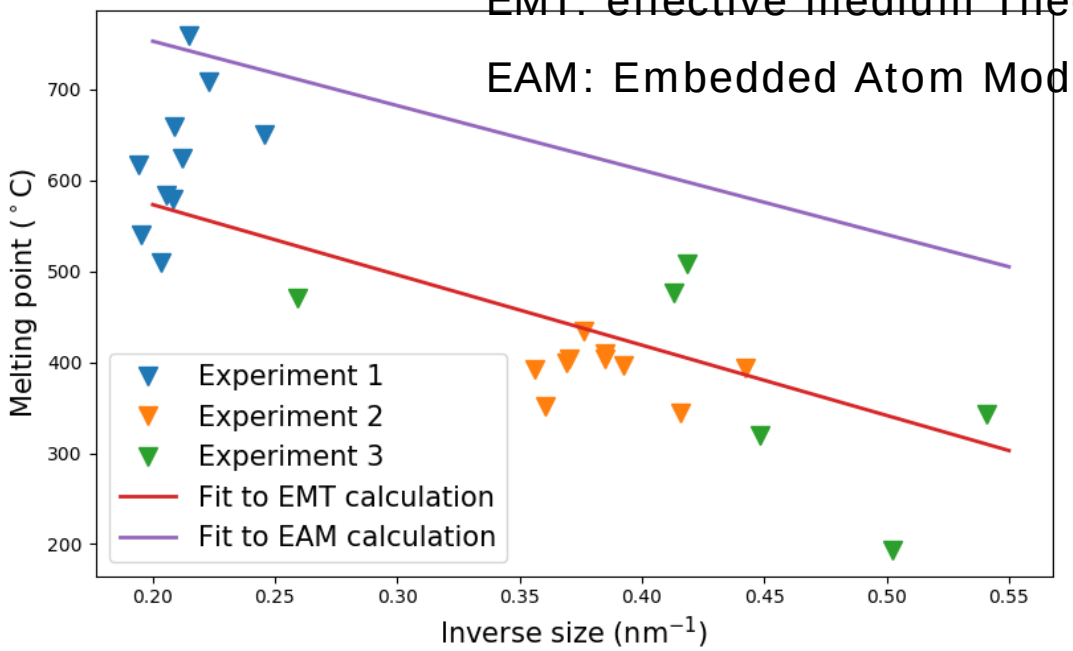
K.K. Nanda, Pramana J. Phys. 72, 617 (2009)

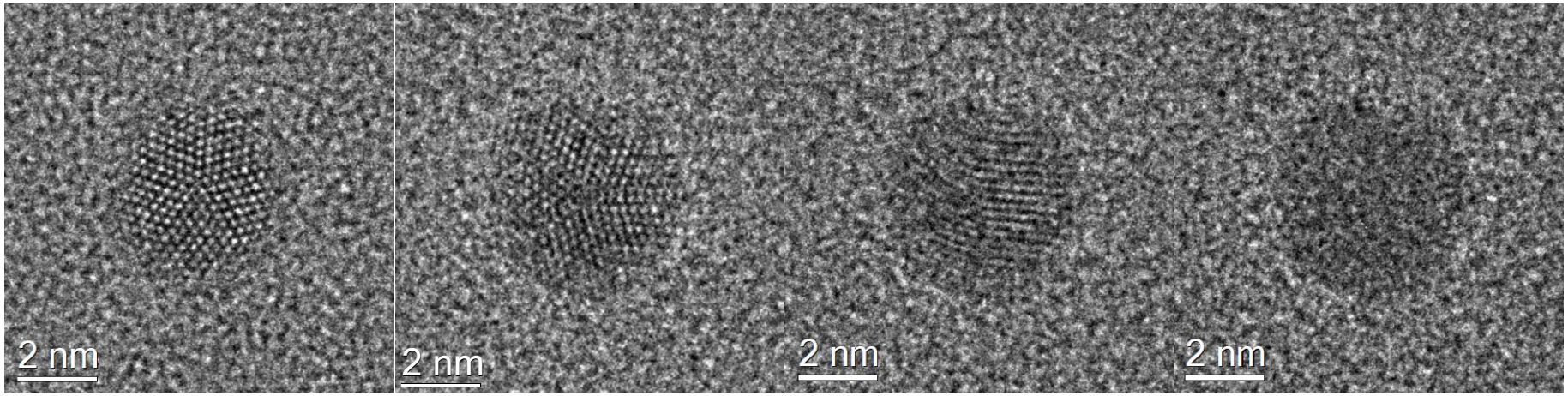
Au@612°C



EMT: effective medium Theory

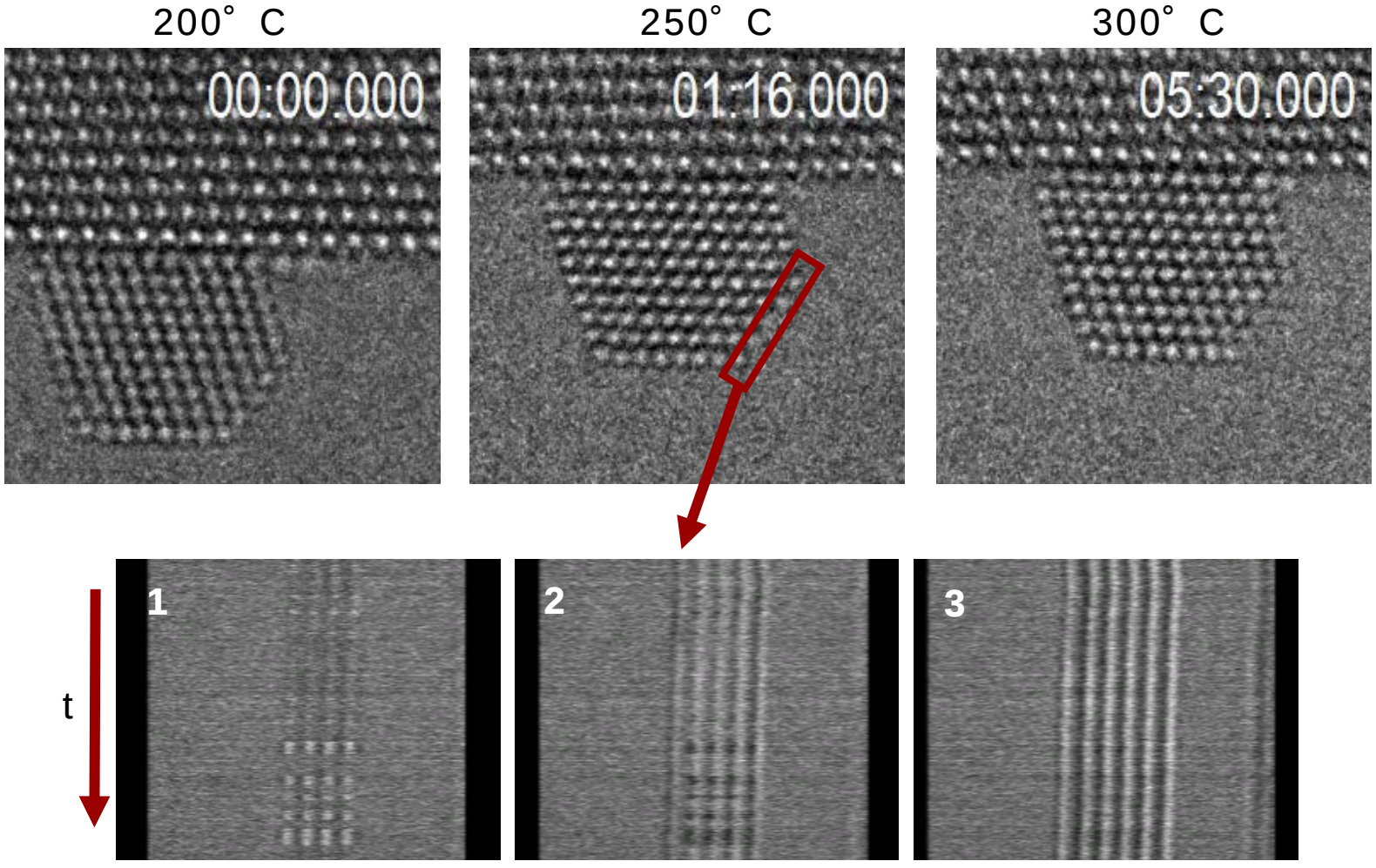
EAM: Embedded Atom Model





P. Schlexer, TWH, *et al.*, *Part. Part. Systems Charac.* 2019 accepted)

Surface Restructuring - Au/CeO_2 4.5 Pa CO

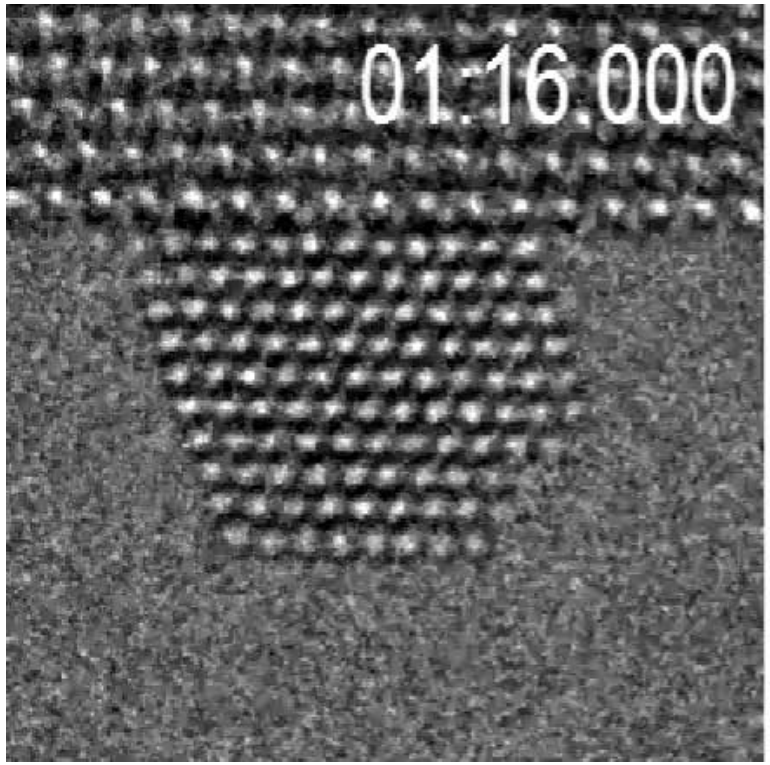


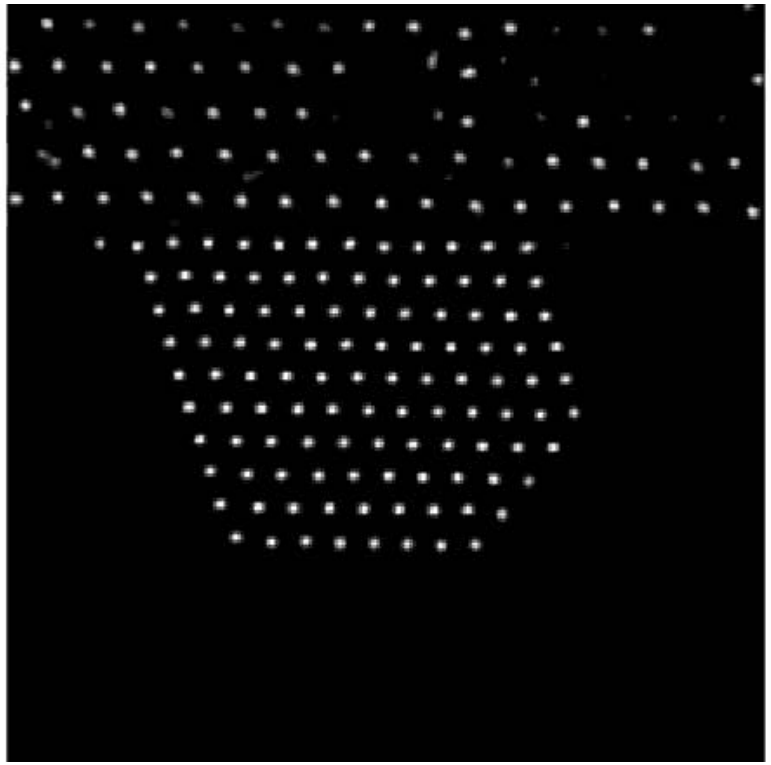
Topmost three layers of the (100) facet @250° C

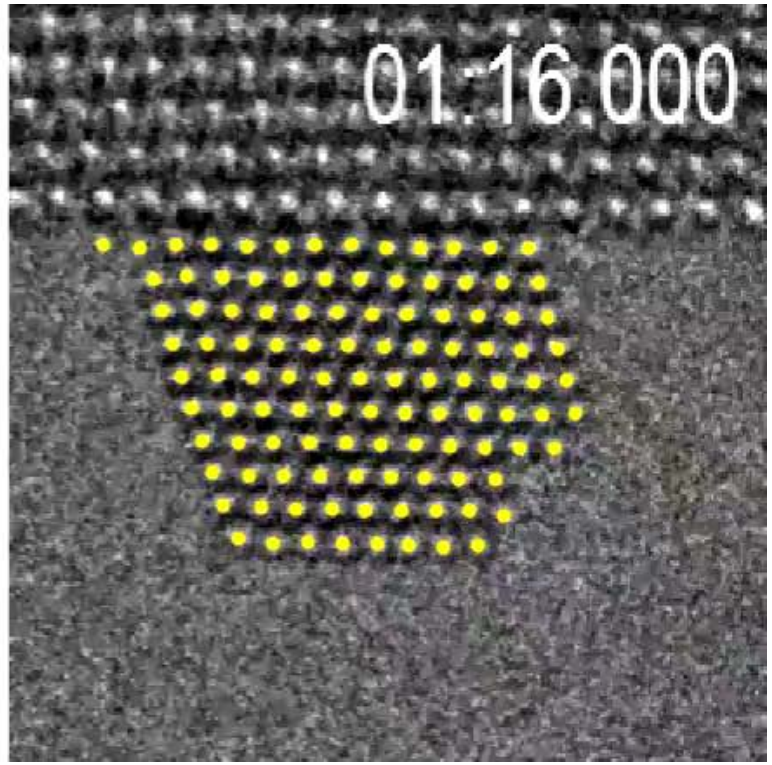
- As the temperature is increased, different surface phenomena are excited
- At 200° C, surface atoms are barely dynamic
- At 250° C, entire layers shift
- At 300° C, The entire surface becomes dynamic and columns on all facets shift in a concerted motion

Data by Pei Liu

Results: Gold Nanoparticle on Ceria







- Concerted diffusion
- Image-corrected 300 keV FEI Titan ETEM (4.5 Pa CO@250°C).

J. Madsen, TWH, *et al.*, *Adv. Theory Simul.* **1**, 1800037 (2018)

Possibilities and Challenges

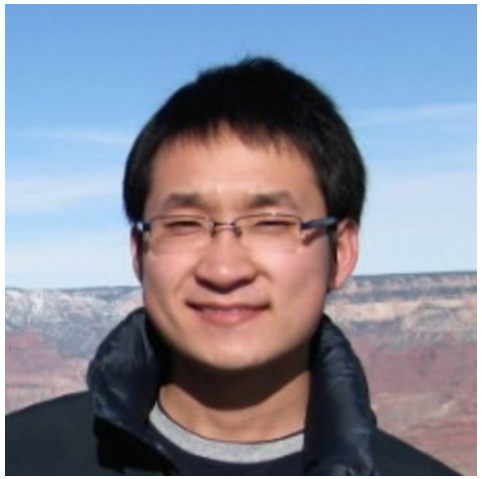
- Sensitivity
  - CMOS and direct electron detection
- High speed data collection
  - Fast data acquisition
  - Data storage
- MEMS heaters
  - High thermal stability
- Correlation of data
  - Interplay with complementary techniques
- Automated analysis
  - Deep learning/neural networks
- Environmental control
  - Contamination
- Local vs. Global effects
  - How are observations dependent on their surroundings
  - Interplay with complementary techniques
- Electron beam effects
  - Low dose
  - High sensitivity
- Data storage
  - Large datasets

Speakers

Judy Cha

- Ph.D. from Cornell
- Post doc at Stanford
- Assistant prof. at Yale

Hanyu Zhang



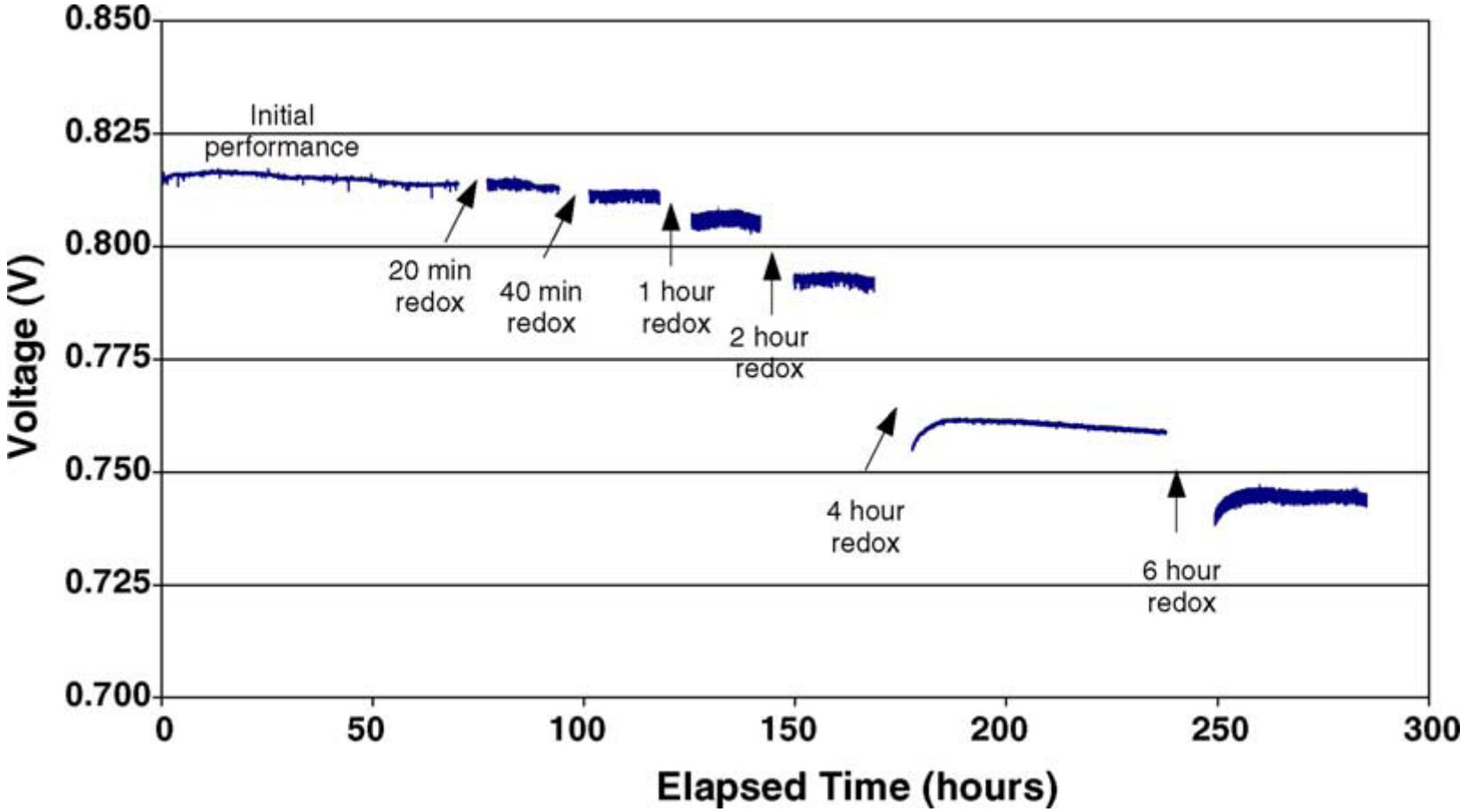
- Ph.D. in Mechanical Engineering, Purdue University in 2016
- Joined NREL as a postdoctoral researcher

Matthew T. McDowell

- Ph.D. Materials Science and Engineering, Stanford University, 2013
- Post doc at Caltech
- Joined Georgia Tech in 2015 as faculty member

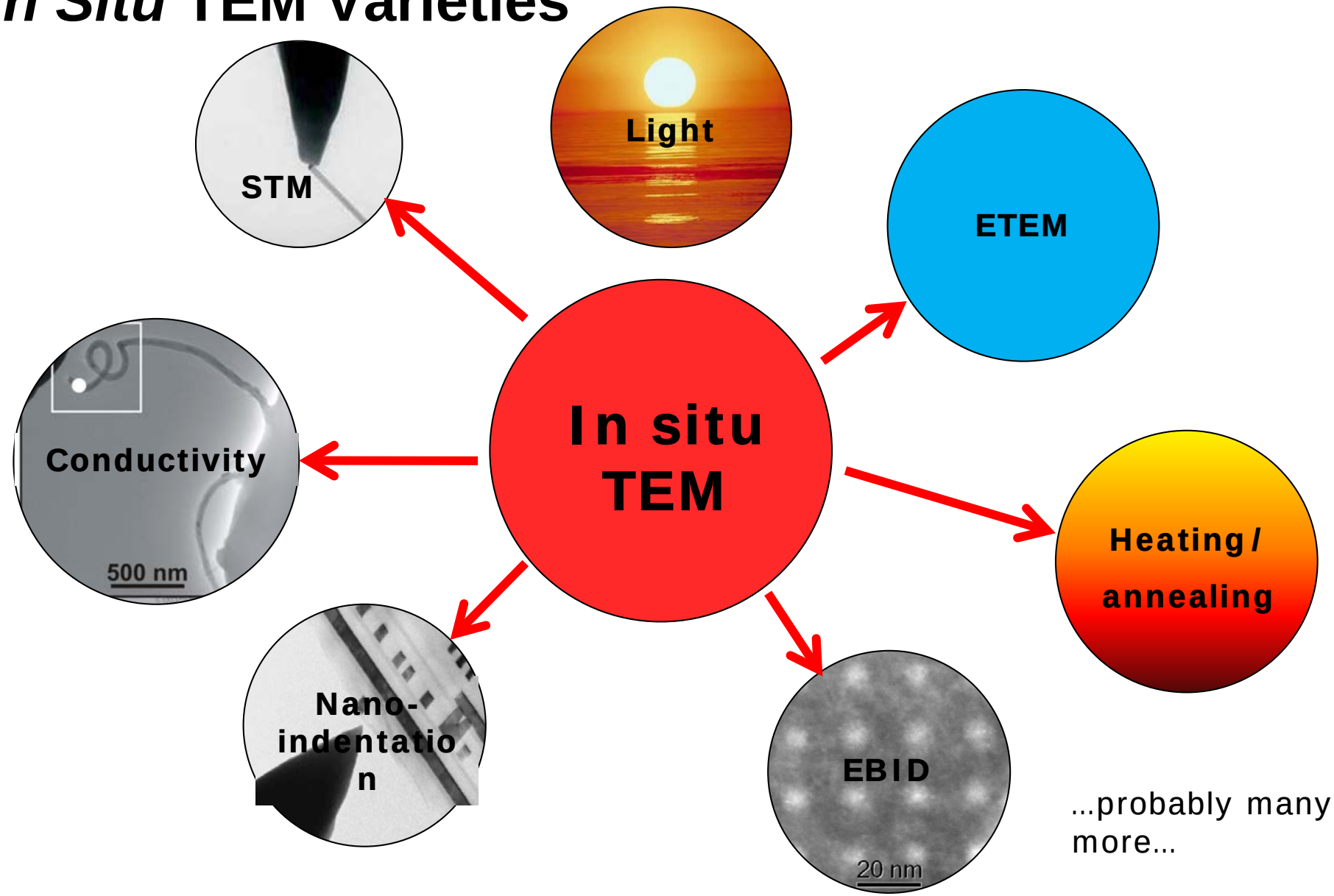
Fuel Cell Anode Failure

- Redox stability of NiO/YSZ based anode



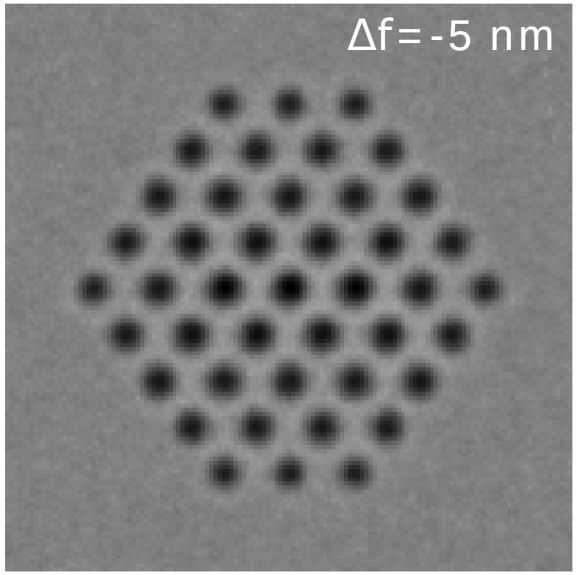
Q. Jeangros, TWH *et al.*, *Acta Mater.* **58**, 4578 (2010)

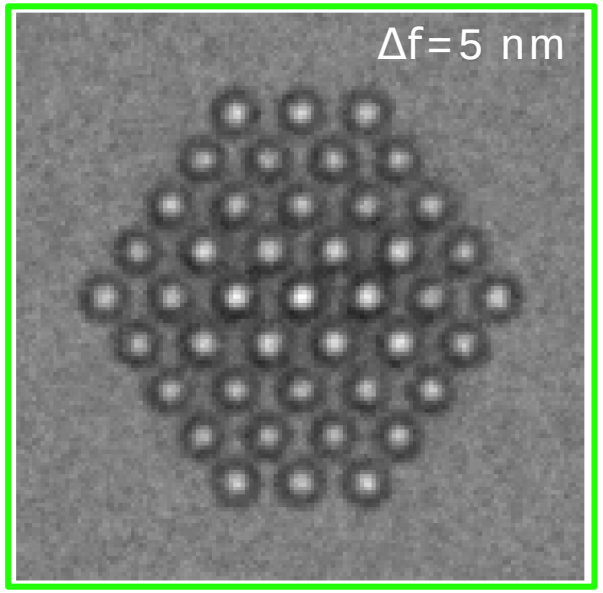
In Situ TEM Varieties

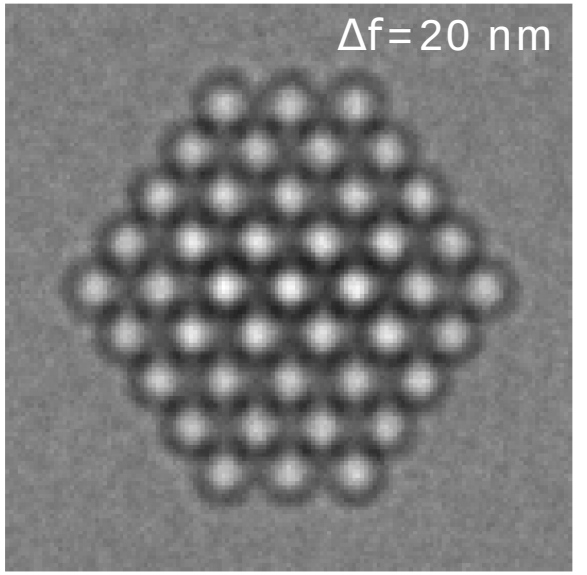


...probably many more...

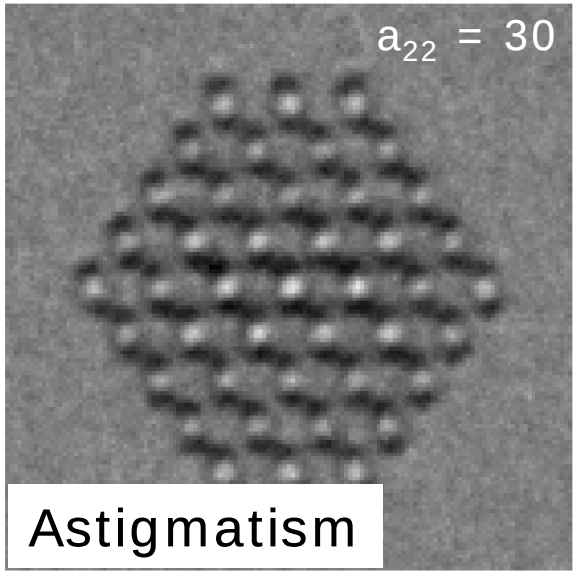
Analyzing HRTEM images is not just peak finding!

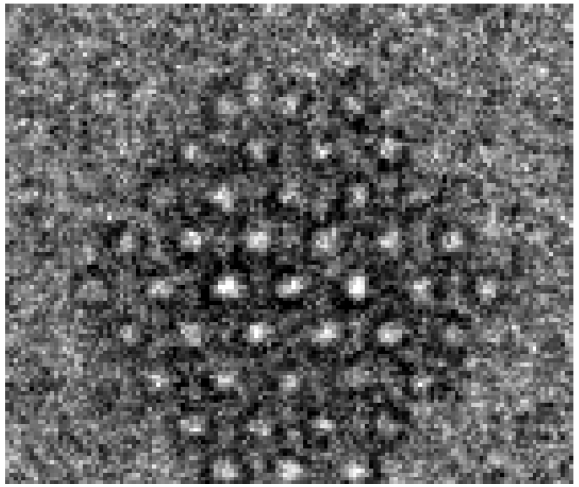


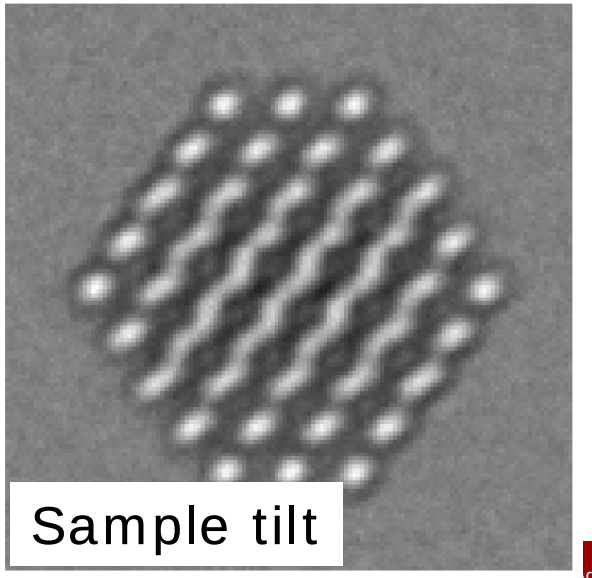




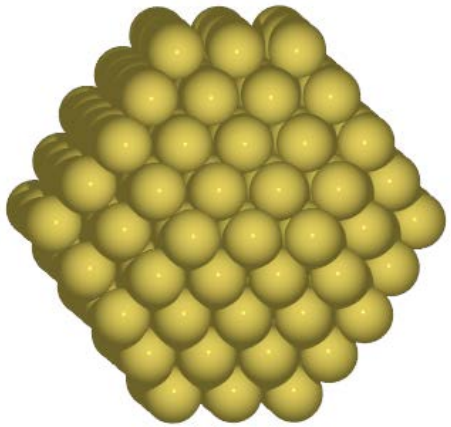
Defocus, height difference and contrast inversion



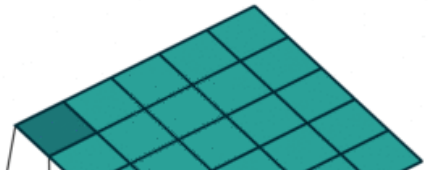


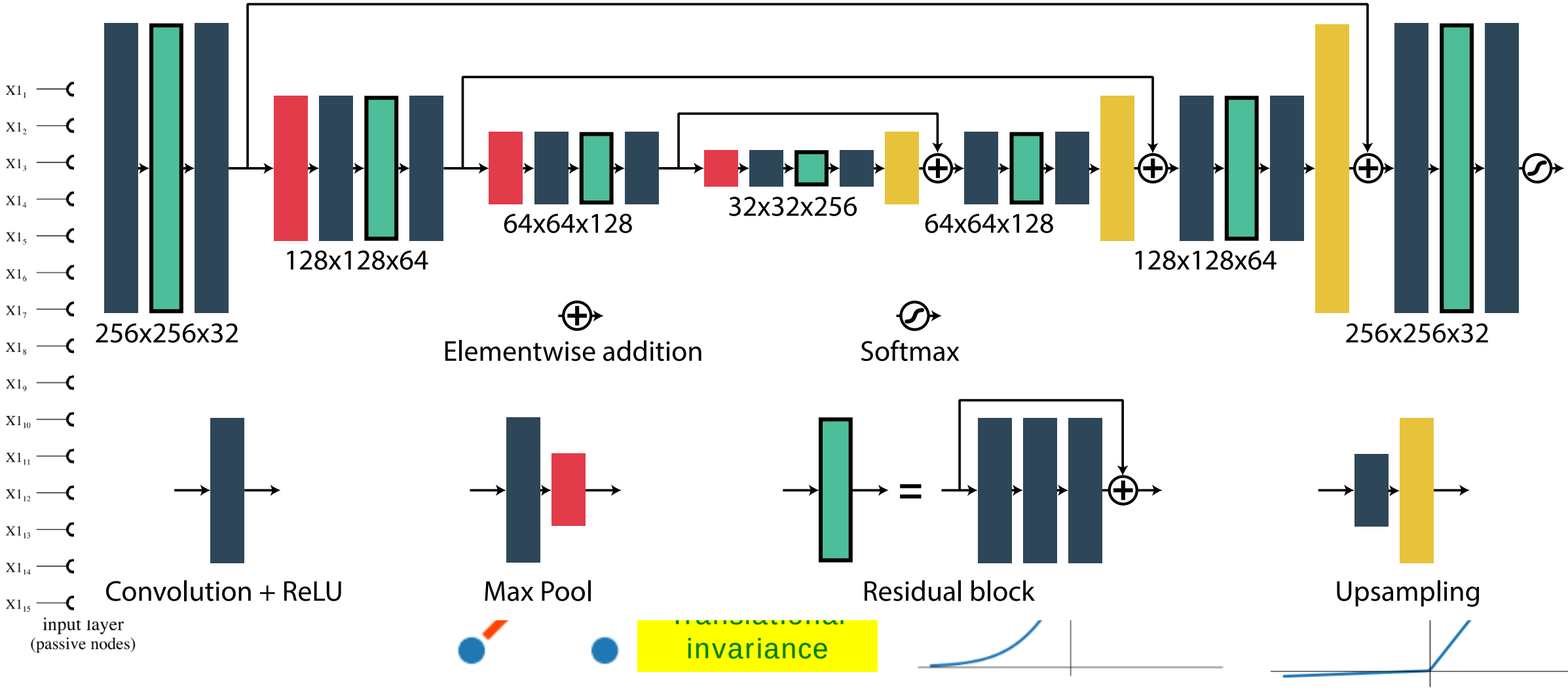


All images on this slide are simulated with PyQSTEM



Convolutional Neural Networks

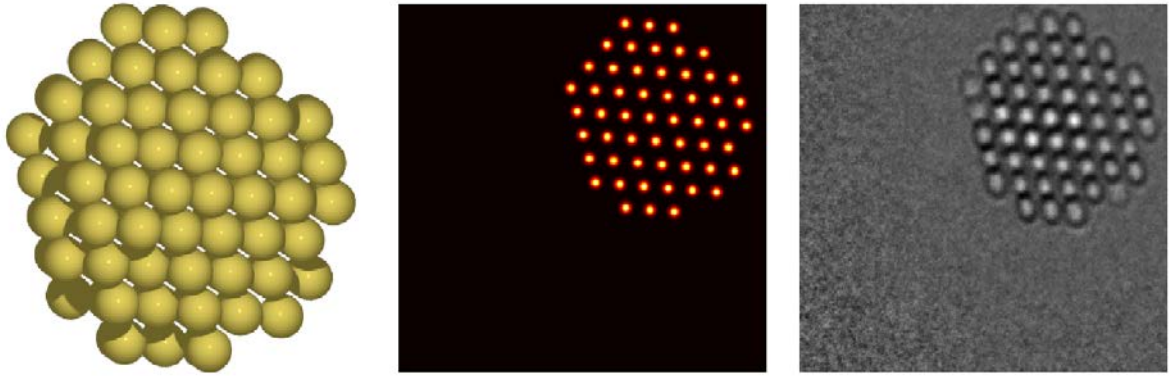


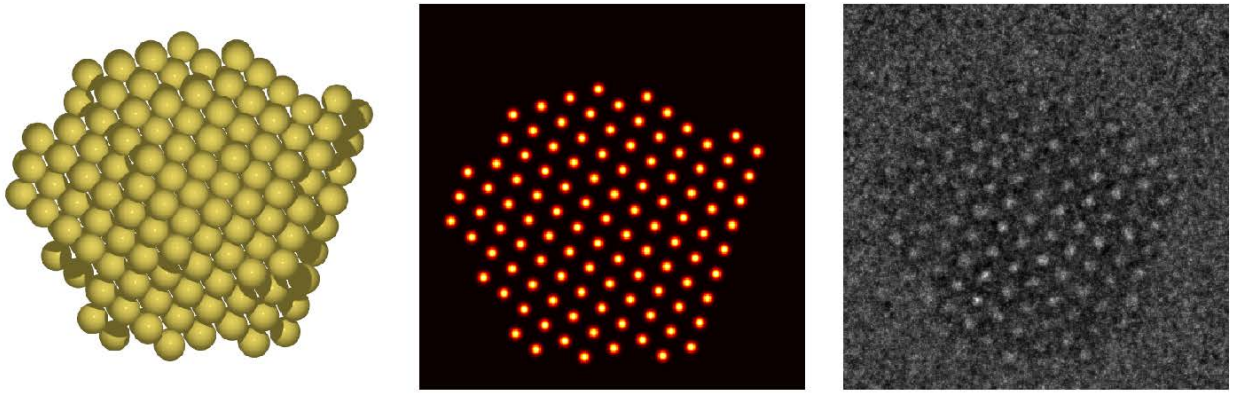


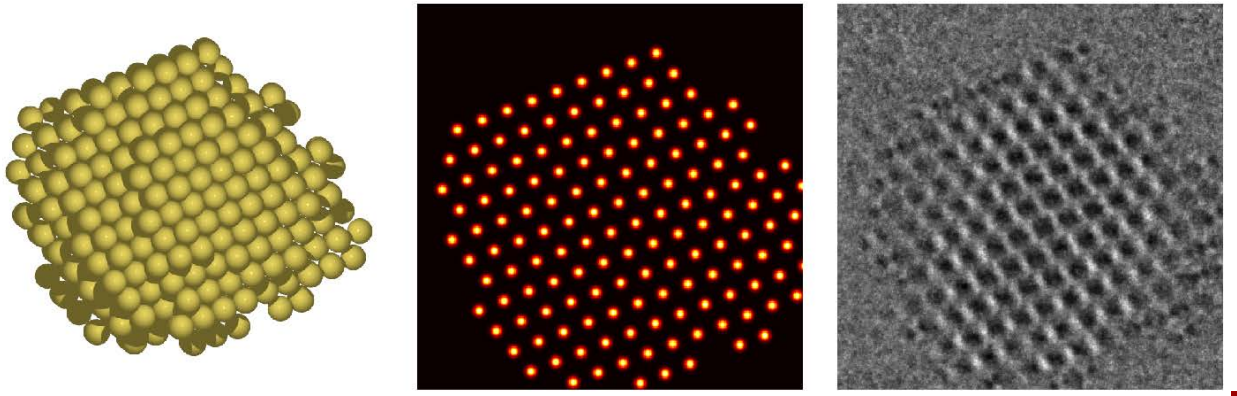
Far fewer weights allow for many more layers!

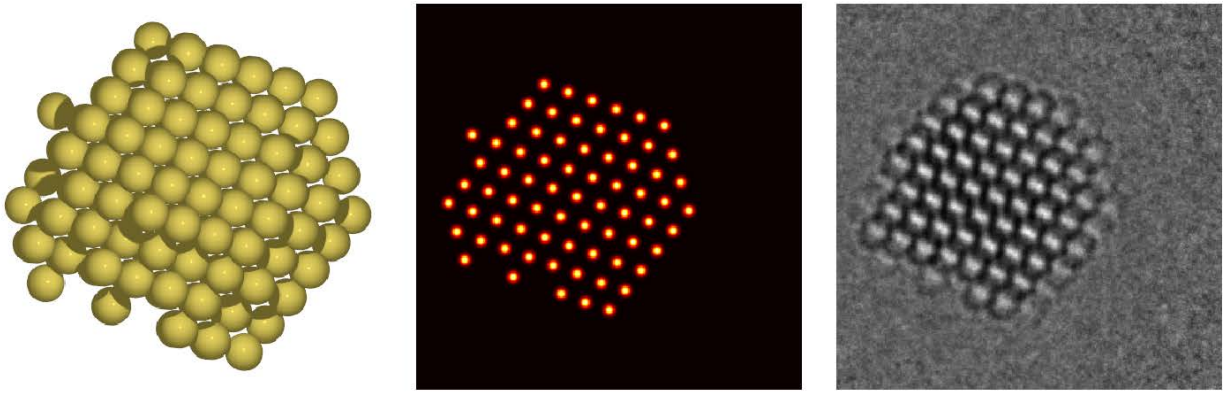
Training the network

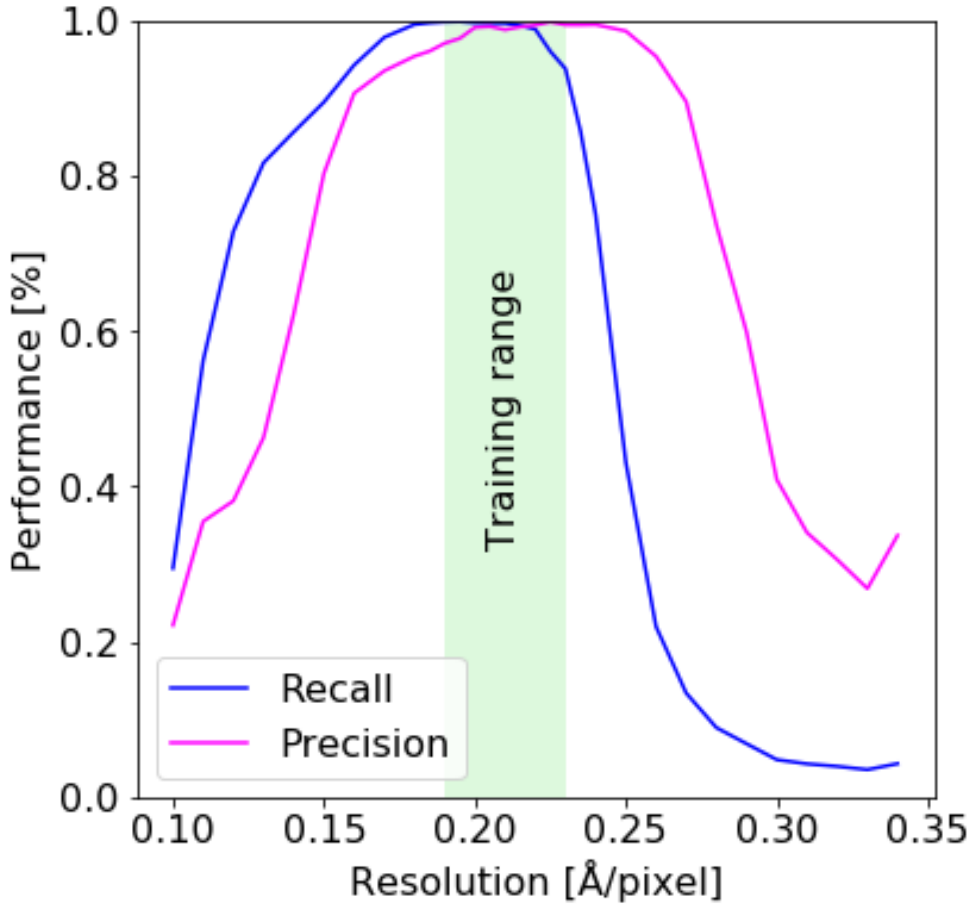
- Training a neural network requires **many** well-labeled examples
  - Typically expensive / hard to produce
- **We can generate simulated HRTEM images for training!**
  - Inexpensive and easy
  - We use PyQSTEM, a Python interface to the QSTEM program by Christoph Koch











Recall: Can it find the atoms?

Precision: Are they correct?

Challenges

- Microscopy parameters and similar structures must be in training set
  - The resolution is critical
  - Vary over all parameters
- Contrast inversions
  - Train to either positive or negative defocus
  - Exception: Some structures like graphene, where the network can learn to recognize the sign of the defocus